Scientific Objective 2: Stratospheric and Mesospheric Chemistry and Transport

The purpose of scientific objective 2 is to test and improve models of stratospheric and mesospheric chemistry and transport.

Introduction

Within the past few years, concern has been expressed as to the ability of man to inadvertently modify the upper atmosphere and, in particular, the ozone content (Molina and Rowland, 1974; Johnston et al., 1976). Any estimates of the impact of anthropogenic emissions on the ozone content must be made with sophisticated atmospheric models (Climatic Impact Committee, 1975; Panel on Atmospheric Chemistry, 1976; Hudson, 1977). The fundamental limits on the accuracies of these estimates are not the reactions or concentrations of the pollutants themselves but rather the knowledge of the many different processes which influence the overall chemical composition, energy budget, and dynamic behavior of the natural atmosphere - as well as the ability to model these complex processes.

Of necessity, therefore, the models employed must use approximations and simplifications in order to make such predictions. The purpose of objective 2 is to provide the information required to test these simplifications and improve the models.

Present Understanding

The structure of the stratosphere and mesosphere is the result of an intricate interplay among a large number of processes which, for simplicity, can be subdivided into the categories of radiation, chemistry, and dynamics. In this section, we will consider the latter two; radiation is considered in objective 3.

In general, a qualitative understanding of the chemistry of the sources, sinks, and budgets of most of the known upper atmospheric constituents now exists. Discussion of upper atmospheric chemistry can be divided into studies of a few families of constituents such as those containing nitrogen, hydrogen, chlorine, and sulfur (Crutzen et al., 1978). These families contain three basic types of species: source molecules (relatively stable compounds), radicals (short-lived derivatives of the source molecules), and sink molecules (more stable forms into which the radicals can be recombined). Concentration profiles of selected upper-atmosphere trace species are shown in figure 1 (Upper Atmosphere Research Satellite Program, 1978).

Stratospheric odd nitrogen, NO_x, is thought to come mainly from the attack of $O(^1D)$ on N_2O which is produced by bacterial denitrification in soils and the ocean (Liu et al., 1977; McElroy et al., 1976). The major sinks for NO_x should be diffusion to the troposphere, followed by rainout of soluble HNO_3 and photodissociation of NO in the upper stratosphere, followed by reaction of $N(^4S)$

with NO to form N_2. Mesospheric odd nitrogen is produced from a variety of ionization and dissociation processes and also from direct dissociation of N_2.

The hydrogen oxide budget is thought to be driven by a near photochemical equilibrium between formation by reaction of $O(^1D)$ and H_2O and destruction (mainly) by reaction of OH and HO_2 to reform H_2O (Liu et al., 1976; Luther and Duewer, 1978). The water budget is probably controlled by two main processes: transport from the troposphere and oxidation of CH_4. Rainout in the troposphere leads to significant reduction of water-vapor concentration with increasing altitudes. Thus, only a small residual penetrates the "cold trap" at the tropopause where a deep minimum in the temperature profile is found. The loss processes are condensation in the troposphere and dissociation in the upper mesosphere, followed by escape of a fraction of the H atoms.

The budget of chlorine is less well-known. The major sources are thought to be CCl_4 and CH_3Cl which are transported to the stratosphere where photolysis produces Cl atoms (Crutzen et al., 1978). Direct injection of HCl into the stratosphere is thought to be less important because of its high solubility in water. Manmade $CFCl_3$ and CF_2Cl_2, photolyzed in the stratosphere, supply an increasing fraction of the injected chlorine. Other halocarbons such as CH_3CCl_3 (methyl chloroform) may be significant sources. The only known sink for the resultant Cl_x is diffusion to the troposphere followed by rainout of HCl.

The atmospheric sulfur cycle is not well understood. Theories suggest that sulfur compounds emitted at ground level in both natural and anthropogenic processes diffuse into the stratosphere where they are oxidized, giving sulfur trioxide which later reacts in the presence of water to form sulfuric acid. It is believed that clusters of sulfuric acid molecules can act as condensation nuclei leading to the growth of stratospheric aerosols which are observed to exist in a 75-percent solution with water and are the principal components of the Junge layer. The sink for sulfur occurs when the heavier aerosols settle out of the stratosphere into the troposphere forming a dilute "acid rain."

The dynamics of the stratosphere below 25 to 30 km are at least crudely characterized and understood from studies of the transport tracers and the extension of tropospheric global circulation models (Johnston et al., 1976; Mahlman and Moxim, 1978). The dynamics of the atmosphere above 30 km is poorly characterized due to the lack of suitable experimental data for testing calculations. Most three-dimensional global circulation models extend to about 30 km; above this altitude, velocity fields are usually deduced from observed pressure and temperature fields or from sparse wind data. Suitable tracers are not available for testing because this is a region of coupled dynamics and chemistry.

The mean meridional winds are toroidal circulations, characterized, for example, at solstice by two cells between equator and pole in the stratosphere, connecting to a single pole-to-pole cell in the mesosphere. The direct cells in the tropics are driven by absorption of solar radiation in the troposphere, with the resulting motions extending high into the stratosphere. The mesospheric cell is similarly generated; thus, both these cells are indirect in that sinking motions take place in the warmer regions. (See fig. 2, from

Cunnold et al., 1975). These motions are clearly the result of a driving force and convert kinetic to potential energy.

The Coriolis torque acting on these meridional motions gives rise to the mean zonal motions. Unlike the meridional motions, these mean zonal motions are in geostrophic balance; that is, the Coriolis force is balanced by the mean horizontal-pressure gradient. As such, they can be deduced from the density field. These zonal motions are not constant in time; the winds have an annual change of direction as the winter and summer poles change places. In addition, a semiannual oscillation in the zonal flow is observed, with maximum westerlies occurring just after the equinoxes and maximum easterlies occurring just after the solstices. There is also a very strong oscillation of the mean zonal wind in the lower tropical stratosphere with a somewhat irregular period that averages out to about 26 months, the so-called "quasi-biennial oscillation." In addition to these cyclic variations, there are a number of irregular short-term and year-to-year variations.

In many respects the testing of both the chemical and the transport models should proceed concurrently. In practice, tests of the models can be devised that will verify either independently. Thus, the basic photochemistry can be tested at altitudes where photochemical equilibrium exists; i.e., the transport lifetimes are short compared to the chemical lifetimes. Measurements of the altitude profile of ozone density can, for example, be used to test photochemical theories above 30 km altitude and used to test the transport models below 30 km.

Currently Available Measurements

Measurements are currently being made in the stratosphere and mesosphere by satellite, balloon, rocket, aircraft, and ground-based experiments. Here we will discuss the satellite measurements only. Current satellite experiments for long-duration observation are focused on the measurement of aerosols and gases involved in the ozone-nitrogen chemistry of the stratosphere. These experiments include the Limb Infrared Monitor of the Stratosphere (LIMS), the Stratosphere and Mesosphere Sounder (SAMS), the Solar Backscatter Ultraviolet/Total Ozone Mapping System (SBUV/TOMS), the Stratospheric Aerosol Measurement II (SAM II), and the Stratospheric Aerosol and Gas Experiment (SAGE). The first four experiments are part of the Nimbus G spacecraft and the last is a Scout launched solo payload. In addition, the SBUV is planned for operational use by the National Oceanic and Atmospheric Administration (NOAA) on the Tiros N payload. Each of these experiments measures a specific parameter or set of gases. The parameters to be measured, the instrument/experiment approach, and the schedule are given in table I.

The Atmospheric Trace Molecules Observed by Spectroscopy (ATMOS) is planned for flight on Spacelab 1. Unlike the others, ATMOS employs a survey instrument technique capable of providing data on a wide range of molecules including the NO_x, HO_x, ClO_x, and O_3 chemistry. However, as it only obtains data at solar occultation, its spatial coverage is limited. The Cryogenic Limb-Scanning Interferometer and Radiometer (CLIR) on the other hand is a limb scanning instrument and will provide global coverage with greater density and time.

Future satellite experiments include the Halogen Occultation Experiment (HALOE), Laser Heterodyne Spectrometer (LHS), and Solar Mesosphere Explorer (SME), followed by the Upper Atmosphere Research Satellite (UARS) experiment to bring together the O_3, NO_x, ClO_x, and solar flux measurements in a simultaneous data set.

Science Requirements

At present, some models treat chemistry and transport independently, whereas others combine these effects. In general the relative emphasis for the latter models will favor one of the processes. Thus, the one-dimensional models contain full chemistry but average all transport using a one-dimensional diffusion constant, while the full global-circulation models have little or no chemistry. Thus the science requirements are varied.

To study the chemistry, we can conveniently look at the families of species. To study those species in photochemical equilibrium, more than one species in the family needs to be measured. In addition, considerably more information can be obtained if the diurnal variation of these species is measured.

Transport in the models can be verified in two ways: first, by observing the densities of conserved quantities such as CH_4, O_3, and N_2O and aerosols below 30 km or the sodium atom above 80 km, and second, by direct observation of the horizontal winds.

Table II (from Upper Atmosphere Research Satellite Program, 1978) gives a list of those species that can be used for the verification of chemistry/ transport models, with the required accuracies and spatial resolutions.

Shuttle Lidar Contribution

Table III gives a list of those species that are proposed for measurement in the experiments sections. In most cases, the resolution and accuracies meet or exceed the requirements given in table II.

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TABLE I.- MEASUREMENTS, APPROACH, AND SCHEDULE OF SATELLITE EXPERIMENTS

RELEVANT TO SCIENTIFIC OBJECTIVE 2

Satellite experiment	Measurements	Instrument/experiment approach	Schedule
LIMS	O_3, H_2O, NO_2, HNO_3, temperature (2 to 4 km resolution; 10 to 70 km altitude)	Limb emission radiometry (6 to 17 μm)	Nimbus G, 1978
SAMS	CO, NO, N_2O, CH_4, H_2O, temperature, wind (15 to 90 km altitude)	Limb emission pressure modulated radiometer (2 to 16 μm)	Nimbus G, 1978
SBUV/TOMS	O_3 (vertical profile greater than 30 km; 5 km resolution; total O_3 maps)	Nadir solar backscatter	Nimbus G, 1978; Tiros N, 1981
SAM II	Aerosol extinction (1 km resolution; 8 to 50 km altitude)	Limb occultation photometer (1 μm)	Nimbus G, 1978
SAGE	O_3, aerosol, NO_2 extinction (1 km resolution; 8 to 65 km altitude)	Limb occultation photometer (0.3 to 1 μm)	AEM-II, 1979
ATMOS	Survey (2 km resolution; 10 to 100 km altitude)	Limb occultation interferometer (2 to 15 μm)	Spacelab 1, 1980; Spacelab 3, 1981
CLIR	Multiple species (2 km resolution; 20 to 140 km altitude)	Limb emission spectrometer/radiometer	Space Shuttle, 1984
UARS	Chemistry; radiation; transport	Variety of instruments	Launch, 1984
HALOE	O_3, HCl, HF, NO, CH_4, H_2O, CF_2, Cl_2, pressure (2 km resolution; 10 to 70 km altitude)	Limb occultation gas filter and broad band radiometer (2 to 11 μm)	Spacelab 3, 1981; ERBSS-A, 1983
LHS	O_3, HNO_3, CF_2Cl_2, $CFCl_3$ (2 km resolution; 10 to 70 km altitude)	Limb occultation laser heterodyne radiometry (9 to 12 μm)	Space Shuttle, 1984

TABLE II.- SCIENCE REQUIREMENTS

Parameter	Altitude range, km	Δx, km	Δz, km	Accuracy, percent
O_3	10 to 60 60 to 90	500	1 3	10 25
NO	25 to 100	500	3	10
NO_2	25 to 60	500	3	10
HNO_3	20 to 30	500	3	10
N_2O	10 to 40	500	3	20
OH	25 to 40 60 to 90	500	3	10 25
H_2O	10 to 70	500	3	10
H_2O_2	25 to 50	500	3	10
HO_2	25 to 50	500	3	10
HCl	20 to 50	500	3	10
ClO	25 to 40	500	3	10
$ClONO_2$	20 to 30	500	3	10
CH_4	10 to 60	500	3	20
CFM's	10 to 40	500	3	20
Na	80 to 100	100	1	10
Aerosols	10 to 100	500	1	30
Wind	15 to 60 65 to 100	1000 1000	3 3	2 m/s 10 m/s

TABLE III.- SHUTTLE LIDAR CONTRIBUTION

Parameter	Altitude range, km	Altitude resolution, km	Accuracy, percent	Lidar experiment
O_3	Stratosphere burden		8	10
	10 to 70	1	2	13
NO	45 to 55	1	20	13
	70 to 150	3	20	25
NO_2	35 to 45	1	10	13
HNO_3	10 to 20	1	10	13
N_2O	Stratosphere burden		1	10
OH	50 to 60	1	20	13
	35 to 100	3	10	21
H_2O	10 to 30	1	2	13
	10 to 40	1 to 5	10 to 20	9
H_2O_2	25 to 35	1	----------	13
HO_2	25 to 35	1	20	13
HCl	Stratosphere burden		10	10
	20 to 30	1	5	13
ClO	30 to 35		20	13
$ClONO_2$	20 to 30		----------	13
CH_4	10 to 20	1	5	13
CFM's	Stratosphere burden		1	10
	10 to 20	1	10	13
Na	80 to 100	1	10	7
Aerosol	10 to 30	1	30	6
Wind	80 to 100	1	5.5 m/s	14
	10 to 30	1	2 to 3 m/s	20

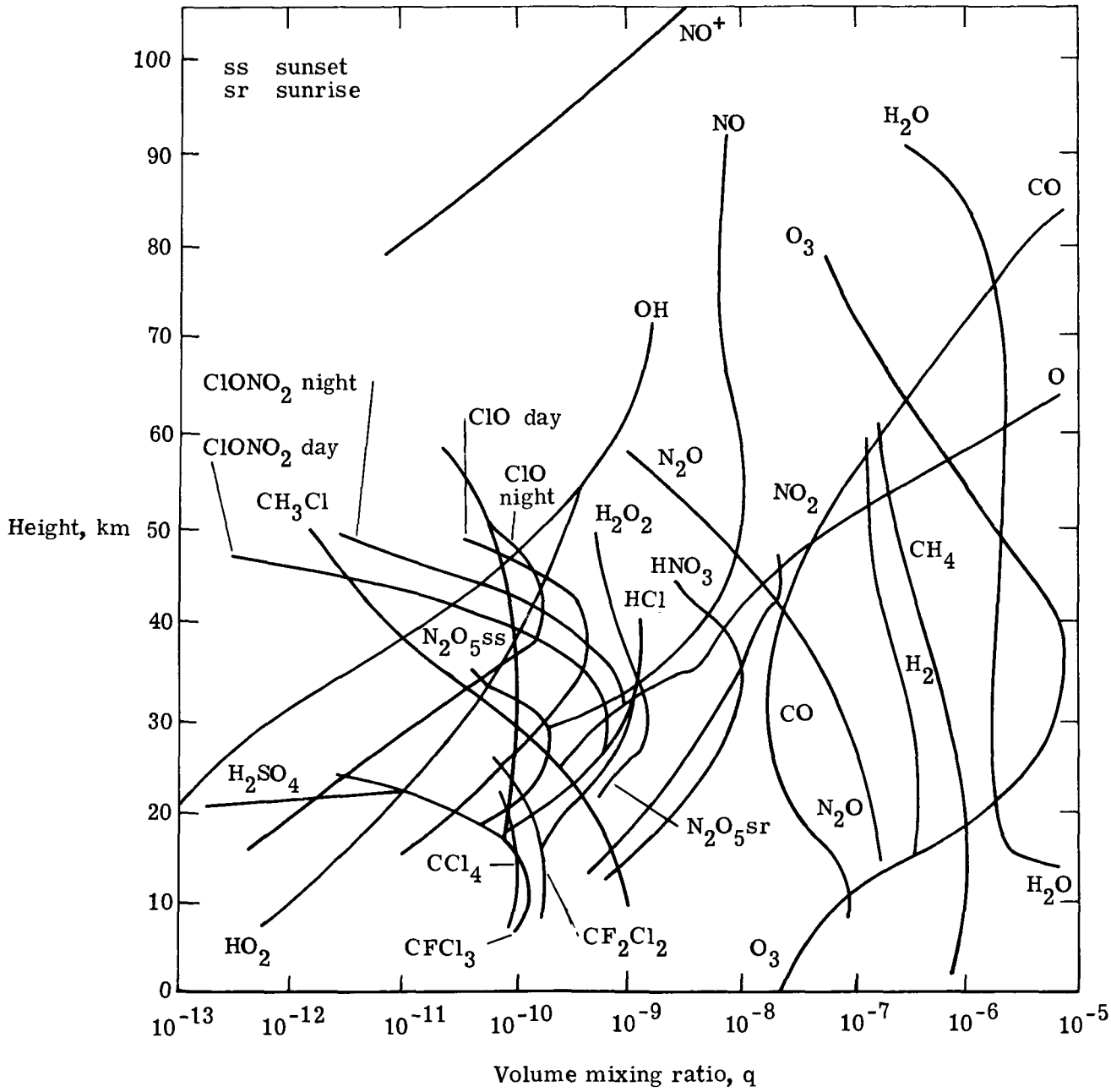

Figure 1.- Concentration profiles of minor species. (From Upper Atmosphere Research Satellite Program, 1978)

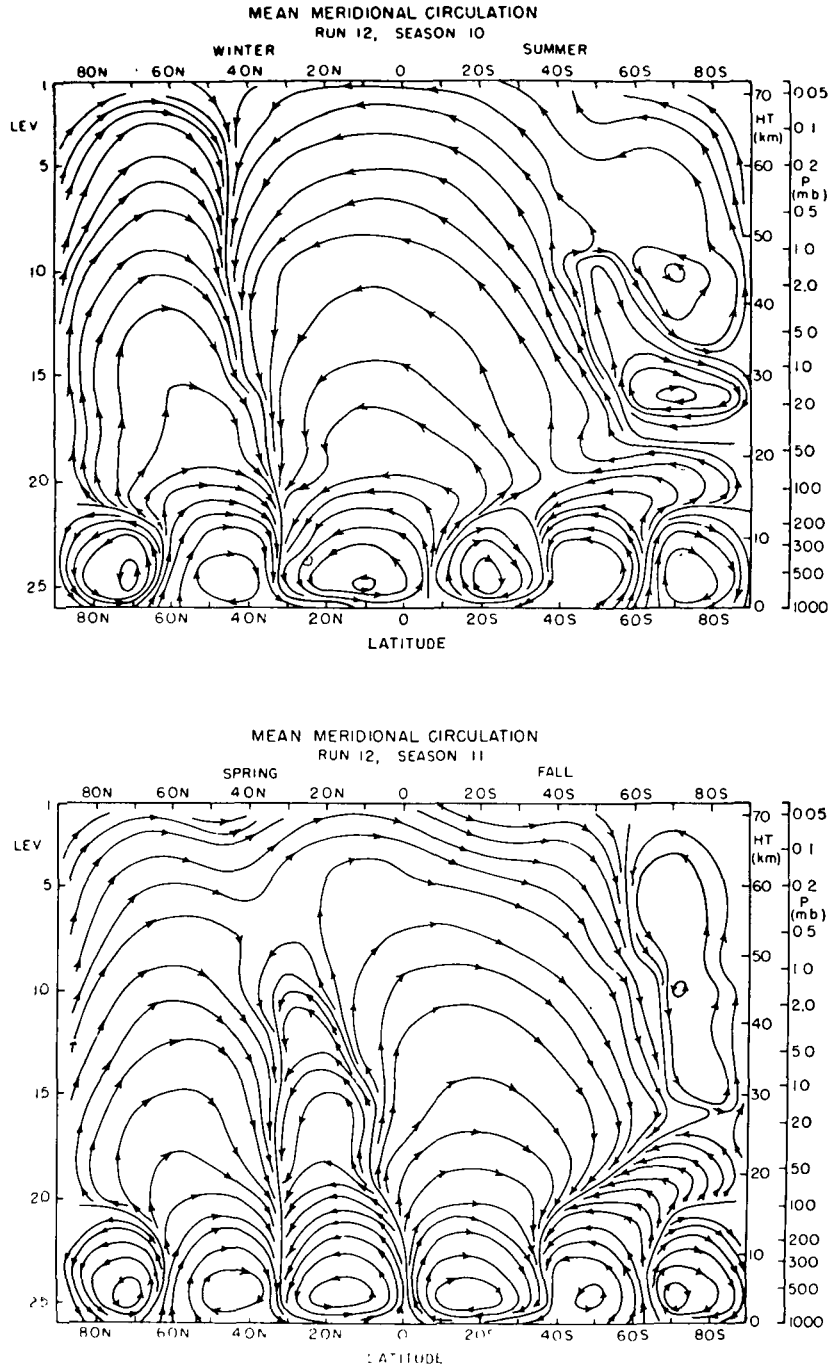

Figure 2.- Mean meridional circulation patterns for the solstices and equinox. (From Cunnold et al., 1975, courtesy American Meteorological Society)